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FOLLOWING PHOTOCHEMICAL REACTIONS BY THERMOGRAVIMETRY

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A new thermal analysis system has been designed to follow the influence of light on solid reactants. This method is based upon the association of a thermogravimetric system for the kinetic measuring method, and a U. V. irradiation system for the activation method. This instrument allows comparative studies of a thermal reaction and the corresponding photochemical one under exactly the same experimental conditions. The experiments, carried out in silver carbonate, have provided new information on photochemical kinetics, but also on solid-state reactivity and even on thermal processes. More generally, this device, designed for studies on reactivity, can be applied to any other system needing the action of light. With the device, the influence of the light intensity, the wavelength and the life-time of light effects on many reactions can be studied.

Thermogravimetric analysis is a particularly suitable method for studying the kinetics of any reaction involving a change in weight. Temperature, gas pressure and composition can be kept constant during the whole chemical process. Moreover, this method gives a direct, continuous and easily interpretable signal. Thus, different heterogeneous reactive systems have been successfully studied by thermogravimetry, and its characteristics, requirements, conditions of use and applications are now clearly known.

On the other hand, the reactivity of crystalline solids is, above all, linked to the presence of lattice defects. Such defects have been established in most decomposition, reduction and oxidation mechanisms. Accordingly, any means of influencing them is worthy of interest; in this respect, light is actually a very interesting parameter for physical chemists, even if they are not photochemists.

In order to study the influence of light on a solid reaction without disturbing other parameters, a thermobalance has been equipped with an optical device which allows direct sample irradiation in the kinetic measurement vessel. It is worth noting that only low quantities of product are required for thermogravimetric measurements, which is a good preliminary condition for homogeneous irradiation of the sample.

At the present time, a review of papers on solid-state photochemical reactions shows that reactions are studied by various experimental methods. Manometric measurements are often carried out, as in the work of Munuera [1, 2] for example, on

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oxygen photoadsorption on titanium dioxide, and the studies of Sood [3] and Prout [4] on the decomposition of nickel and lithium azides respectively, by nitrogen release. The main drawback of this method is the increase of pressure, which may have a very important effect upon solid properties and reactivity. Other methods, such as the measurement of conductivity [5–7], are more especially used to follow sample change during an experiment, but they rarely give absolute results and thus are not suitable for the comparison of experiments carried out under different conditions.

Design of the experimental device

As the sample is located in the middle of the furnace of the microbalance and because of the heating conditions, it was impossible to place the U. V. source next to the sample. Thus, an optical device appeared to be absolutely necessary to conduct a beam of sufficient intensity from the outside onto the sample. As already mentioned, the sample is located in the middle of the furnace; it can only be reached by means of a vertical movement of the furnace. In order to obtain the best reproducibility, the optical device is fixed to the furnace and moves along with it. Thus, the light beam is adjusted once and for all, and does not have to be modified for each experiment.

Figure 1 shows the device, which is provided with:

- a microbalance (1),
- quartz suspensions and small quartz containers (2),

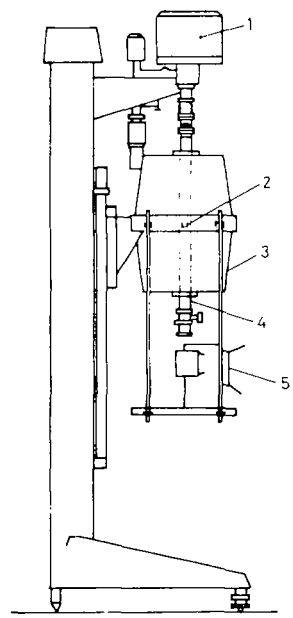

Fig. 1 General view

– a furnace (3),
– quartz tubes (4),
– and the optical device (5).

Figure 2 shows the lamp (A) (a 350 W mercury arc lamp) located in a protective housing (B) provided with a cooling fan and a condensing system (C). A liquid-filter (D) reduces unwanted infrared and its consequent heat. The output light intensity can be reduced by an iris-diaphragm (E). The wavelength is selected by inserting filters, which are carried by a filter holder (F). A 90° light tube (G) deflects the output beam perpendicularly to the lamp housing optical axis, through a quartz window (H) at the bottom of the vessel tube. The deflected beam is then condensed onto the sample by a spherical mirror (I) placed upon it.

Both systems (optical and measuring systems) are sufficiently independent to be used separately; for example, a pure thermal reaction can be studied under exactly the same experimental conditions as a photochemical reaction.

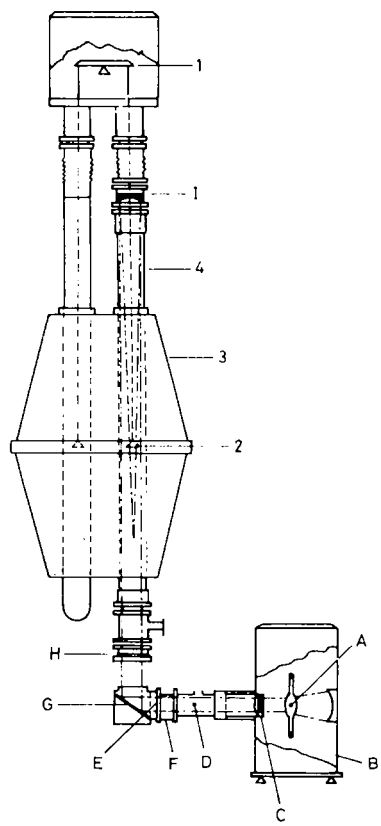

Fig. 2 Optical device

Test of the apparatus

The efficiency of this apparatus has been tested on the photochemical decomposition of silver carbonate. This product has already been studied appreciably in our laboratory [8, 9] under exclusively thermal conditions. Moreover, like all other silver salts, silver carbonate is known for its sensitivity to light [10]. It appeared interesting to compare silver carbonate decomposition kinetics under new conditions – i.e. photochemical ones – with those of the well-known thermal decomposition.

All authors agree that the product of thermal degradation is silver oxide [8–10], even though Drake and Benton [11] demonstrated its thermodynamic instability; although the calculated oxygen equilibrium pressure at 169° is 150 torr, the oxide remains the final product whatever the pressure; metallic silver is obtained only at higher temperatures (300°). This metastability was very interesting for us, and more especially as there are conflicting results concerning the sensitivity to light of the oxide; some authors agree on its occurrence [12–14], while others do not [15, 16].

Effect of light on silver carbonate stability

The loss of weight during a linear temperature programme is shown in Fig. 3. There is a striking difference between the temperatures at the beginning of the reaction with light and without. In this experiment, under 30 torr carbon dioxide pressure, silver carbonate under purely thermal conditions decomposes only at 100°, whereas under irradiation the reaction takes place at room temperature.

Effect of light on silver carbonate decomposition kinetics

Under the conditions required for silver carbonate thermal decomposition, light enhances the reaction efficiency by a factor of 10 (Fig. 4).

Moreover light reduces the activation energy from 20 kcal per mole (pure thermal decomposition) to 6 kcal per mole (photochemical decomposition).

Influence of light intensity on silver carbonate decomposition kinetics

Figure 5 shows the reaction rate vs. light intensity. It appears that there is no direct proportionality: for the lowest intensities (0 to 70 percent of the output light) the rate is not particularly dependent upon this parameter. This can perhaps be analysed as a threshold phenomenon; there is proportionality in the middle of the intensity scale, whereas a sort of saturation effect seems to appear for the highest values.

The instrument has been designed to allow alternate exposure to light and darkness. Some experiments have been carried out to observe the life-time of light effects in solids; the results are summarized in Figs 6 and 7. It is to be observed that the weight change between two light periods is very similar to that during pure thermal decomposition. In other words, the "catalytic" effect of light seems to disappear as soon as the irradiation stops.

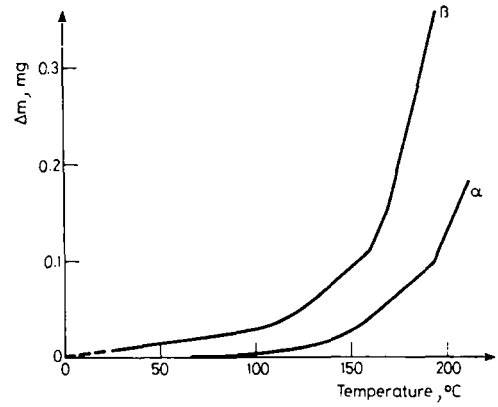

Fig. 3 Thermal and photochemical decomposition under linear temperature programme. P_{CO_2} = 30 torr, α = without irradiation, β = with irradiation

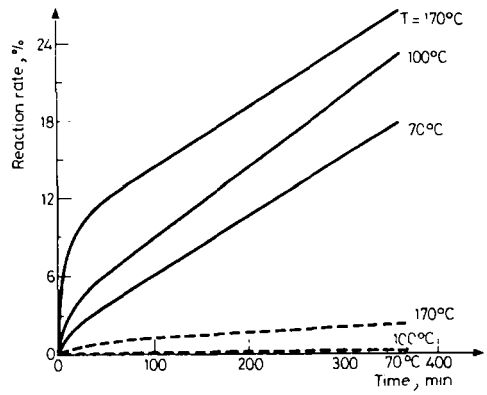

Fig. 4 Effect of light on silver carbonate decomposition kinetics. P_{CO_2} = 30 torr, -- - — without irradiation, —— with irradiation

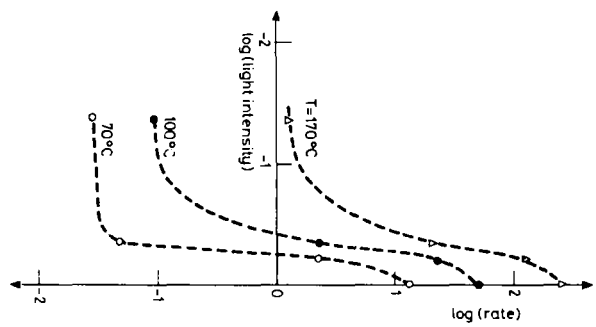

Fig. 5 Influence of light intensity

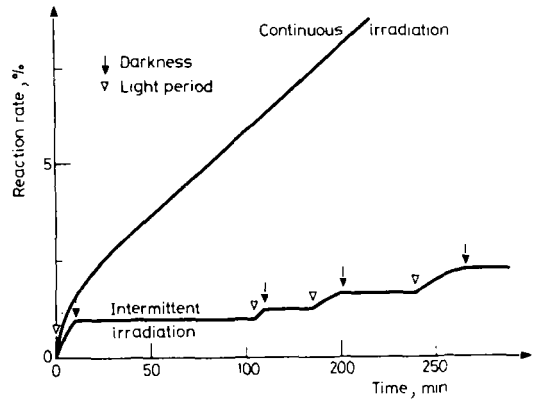

Fig. 6 Influence of alternate exposure to light and darkness. $T = 70°$, $P_{CO_2} = 30$ torr

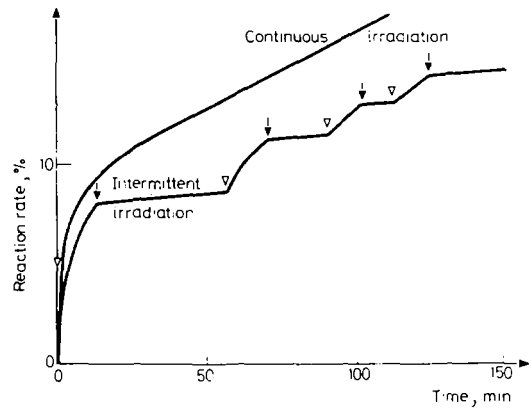

Fig. 7 Influence of alternate exposure to light and darkness. $T = 170°$, $P_{CO_2} = 30$ torr

Conversely, for the same reaction rate, a comparison of decompositions under continuous and discontinuous irradiation shows that the latter is the more efficient. It seems that when irradiation is resumed after a period of darkness, the photochemical process is stimulated.

Influence of the wavelength

The silver carbonate absorption spectrum presents a maximum in the range of 430 to 220 nm. Figure 8 shows the reaction rate vs. time for various irradiation conditions.

Curves 1 and 2 are reference experiments,

1 – experiment under complete output irradiation,
2 – experiment without irradiation,

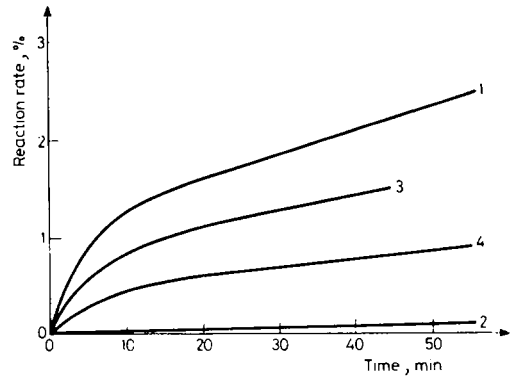

Fig. 8 Influence of the wavelength. $T = 100°$, $P_{CO_2} = 30$ torr, 1 — reference with total irradiation, 2 — reference without irradiation, 3 — with filter cutting off above 270 nm, 4 — with filter cutting off above 400 nm

3 — experiment with a filter cutting off the radiation above 270 nm,
4 — experiment with a filter cutting off the radiation above 400 nm.

A decrease in the reaction rate can be observed between experiments 1 and 3, but in our opinion this is only a consequence of the stepping-down of intensity due to the insertion of a filter. Curve 4 was expected nearer to curve 2 (without irradiation), but it must be borne in mind that the whole absorption zone is not completely removed by filter 4.

Conclusion

This instrument, which has been successfully applied to the study of silver carbonate kinetics, could easily be applied to many other reactive solid substances. The results obtained in the field of photochemical decomposition provide new information, useful even for the knowledge of pure thermal decomposition mechanisms.

This first test has been positive and allows us to contemplate numerous applications. As a reminder, with this device reactions involving a loss or gain of weight can be followed; because of the presence of a mirror in the vessel, a corrosive atmosphere should be avoided, and moderate temperatures are recommended. The main feature of this device is that it allows direct and continuous observation of the effects of light; the optical and measuring system are sufficiently independent to be used separately; it is thus possible to follow a reaction without any irradiation, or under continuous of intermittent irradiation. In the same way, the atmosphere in the reaction vessel pressure, temperature, composition is controlled with precision, so that many comparative studies can be carried out in which only one parameter is changed at a time.

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Zusammenfassung — Ein neues thermisches Analysensystem zur Untersuchung der Einwirkung von Licht auf feste Reaktanden wird beschrieben. Die Methode beruht auf einer Kombination eines thermogravimetrischen Systems für kinetische Meßmethoden mit einem UV-Bestrahlungssystem für die Aktivierungsmethode. Das Gerät ermöglicht vergleichende Untersuchungen einer thermischen und der entsprechenden photochemischen Reaktion unter gleichen Versuchsbedingungen. An Silbercarbonat ausgeführte Untersuchungen haben neue Informationen über die photochemische Kinetik, aber auch über die Festkörperreaktivität und sogar über thermische Prozesse ergeben. Allgemeiner gesagt, das für Reaktivitätsstudien konstruierte Gerät kann auch zur Untersuchung anderer die Einwirkung von Licht erfordernden Systeme benutzt werden. Mit dem Gerät können der Einfluß der Lichtintensität, der Wellenlänge und der Wirkungsdauer der Lichteffekte auf viele Reaktionen untersucht werden.

Резюме — Разработаны новые термоаналитические системы, позволяющие исследовать влияние света на твердые реагирующие вещества. Основой является соединение термогравиметрической системы в методе измерения кинетики с УФ облучательной системой в методе активации. Установка позволяет проводить сравнительные исследования термической реакции и соответствующей фотохимической реакции при точно одинаковых экспериментальных условиях. Эксперименты, проведенные с карбонатом серебра, позволили получить новую информацию не только о кинетике фотохимических реакций, но также о реакционной способности вещества в твердом состоянии и о различных термических процессах. Более того, эта установка может быть присоедина к другой какой-либо системе для изучения действия света и с помощью которой может быть изучено влияние интенсивности света, длины волны и продолжительность действия света на многие реакции.